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Force-compensated hydrogel-based pH sensor

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ABSTRACT

This paper presents the design, simulation, assembly and testing of a force-compensated hydrogel-based pH sensor. In the conventional deflection method, a piezoresistive pressure sensor is used as a chemical-mechanical-electronic transducer to measure the volume change of a pH-sensitive hydrogel. In this compensation method, the pH-sensitive hydrogel keeps its volume constant during the whole measuring process, independent of applied pH value. In order to maintain a balanced state, an additional thermal actuator is integrated into the close-loop sensor system with higher precision and faster dynamic response. Poly (N-isopropylacrylamide) (PNIPAAm) with 5 mol% monomer 3-acrylamido propionic acid (AAmPA) is used as the temperature-sensitive hydrogel, while poly (vinyl alcohol) with poly (acrylic acid) (PAA) serves as the pH-sensitive hydrogel. A thermal simulation is introduced to assess the temperature distribution of the whole microsystem, especially the temperature influence on both hydrogels. Following tests are detailed to verify the working functions of a sensor based on pH-sensitive hydrogel and an actuator based on temperature-sensitive hydrogel. A miniaturized prototype is assembled and investigated in deionized water: the response time amounts to about 25 min, just half of that one of a sensor based on the conventional deflection method. The results confirm the applicability of the compensation method to the hydrogel-based sensors.

Keywords: Force compensation, closed-loop control, microelectromechanical systems (MEMS), hydrogel, thermal actuator, pH sensor.

1. INTRODUCTION

In hydrogel-based micro sensors [1, 2] (Fig. 1), the hydrogel serves as the sensing element in the analyte solution by changing its volume and generating a sensing pressure p_{sens} in response to the solution concentration change Δc . Then the mechanical transducer transfers p_{sens} into an analytical output signal y . This sensor is in open-loop state with a transfer function $f(\Delta c)$. One drawback for this sensor is a long response time due to the large diffusion coefficient D_{coop} [3], when the measuring solution diffuses into the cross-linked polymer chains and determines hydrogel swelling kinetics. Furthermore, because of the visco-hyperelastic material properties, hydrogel shows creep and relaxation phenomena, leading to poor long-term stability and reproducibility [4]. Thus, there is a strong motivation to mitigate those adverse effects in the hydrogel-based micro-sensor.

Fig. 1. (a) Schematic illustration and (b) working principle of the hydrogel-based micro-sensor

Two material-based strategies have been utilized to solve this problem: modified hydrogel material properties [5-9] (e.g. polymer type, monomer ratio etc.) and reduced hydrogel structure dimension [10] (e.g. thin layer, small hydrogel particles instead of bulk material etc.). Besides, the transducer itself was optimized, for instance, the bending plate of a piezoresistive pressure transducer was perforated with circular holes to raise the sensitivity [11].

From a certain perspective on control, micro electromechanical systems (MEMS) can be divided into open- and closed-loop devices [12]. While the sensor using open loop control (e.g. deflection method) is simple and low-cost, the sensor using closed-loop control (e.g. compensation method) offer higher precision and faster dynamic response. Previously we [13, 14] introduced a system-based compensation approach to overcome the challenges described above. By

implementing a closed-loop sensor system, a compensated force/pressure, which is generated on the hydrogel-based sensor, becomes the sensor output signal instead of the output voltage which remains constant due to the constant volume of hydrogel, independent of applied analytic solution.

This paper presents an advanced force-compensated hydrogel-based pH sensor to improve the response time. In order to miniaturize the device, a likewise hydrogel-based actuator replaces the macroscopic pressure source in [13] to provide the compensation force.

2. THEORY AND DESIGN

2.1 Working principle

Fig. 2 demonstrates the working principle as well as the device structure of this force-compensated hydrogel-based pH sensor. In response to the pH change in the aqueous solution, the pH-sensitive hydrogel changes its volume and generates a sensing pressure p_{sens} . The piezoresistive pressure sensor is utilized as a chemical-mechanical-electronic transducer to transfer p_{sens} into electrical output voltage V_{out} . An additional thermal micro-actuator with a temperature-sensitive hydrogel is added on the sensor to generate a temperature induced pressure p_{comp} , which is ultimately adjusted to be equal to p_{sens} . Through the compensation method, the volume of this pH-sensitive hydrogel is kept constant during the whole measuring process, independent of the applied pH value. In addition, the temperature value T from the thermal actuator becomes the actual sensor output signal, which has a corresponding relation to the pH value in the analyte solution ($T = f(\text{pH})$).

Fig. 2. Hydrogel-based pH sensor with force compensation via a temperature-sensitive hydrogel: (a) working principle, (b) 3D structure and (c) cross-section structure

2.2 Sensor design

In principle, the micromachining piezoresistive pressure sensor ($5 \times 5 \times 0.4 \text{ mm}^3$) (EPCOS, Germany) with a $20 \text{ }\mu\text{m}$ bending plate comprises four piezoresistors to get a full Wheatstone bridge circuit (fig. 3a). Since the temperature-sensitive hydrogel and the water approach the top surface of the pressure sensor directly, a thin PDMS layer ($7 \text{ }\mu\text{m}$) (Sylgard 184, Dow Corning, USA) is spun on the surface to avoid short circuit. The silicon cap ($4.6 \times 5 \times 0.3 \text{ mm}^3$) is fabricated by bulk micromachining process, including PECVD- Si_3N_4 , RIE- Si_3N_4 , wet etching and photolithography (fig. 3b). The hydrophilic Al_2O_3 membrane (Anapore, Whatman, USA) with a pore diameter of 200 nm not only serves as a fixed boundary for the hydrogel but also allows water transport to hydrogel surface (fig. 3e). A Peltier module ($5 \times 5 \times 2.3 \text{ mm}^3$) (uwe electronic, Germany) provides heat loading to the temperature-sensitive hydrogel. Polyvinyl alcohol

(PVA) with Polyacrylic acid (PAA) (Sigma-Aldrich, USA) serves as pH-sensitive hydrogel layer ($1 \times 1 \times 0.04 \text{ mm}^3$) (fig. 3c). Poly-N-isopropylacrylamide (PNIPAAm) (Sigma-Aldrich, USA) with 5 mol% monomer 3-acrylamido propionic acid (AAmPA) is synthesized as the temperature-sensitive hydrogel with a wide range of temperature response from 20 to 60 °C. For the purpose of getting faster dynamic response, PNIPAAm is stirred into particles with a diameter of less than 50 μm (fig. 3d).

Fig. 3. Microscope photos and SEM images of (a) the pressure sensor, (b) the silicon cap, (c) the pH-sensitive hydrogel layer under the pressure sensor, (d) the temperature-sensitive hydrogel particles and (e) the hydrophilic Al_2O_3 membrane

3. SIMULATION

3.1 Theory

As for this hydrogel-based sensor, the governing equations relating the heat transfer rate and the temperature gradient for the heat transfer mechanism include[15]

thermal conduction

$$q''_{\text{cond}} = \frac{Q}{A} = -k \frac{dT}{dx} \quad (1)$$

and thermal convection

$$q''_{\text{conv}} = \frac{Q}{A} = -h(T_s - T_f), \quad (2)$$

with Q the heat flow, q''_{cond} the conduction heat flux (W/m^2), q''_{conv} the convection heat flux (W/m^2), k the thermal conductivity (W/mK), h the convective heat transfer coefficient ($\text{W}/\text{m}^2\text{K}$), T_s the temperature of the surface, T_f the temperature of the fluid (in this case, the air), T_s the absolute temperature (K) of a surface and A the section area for the heat transfer (m^2).

3.2 Simulation result

Since the cavity in the silicon cap is totally filled with hydrogel particles and water, hydrogel is presumed to have the same thermal conductivity as water. For the finite element simulation we assume the following boundary conditions and loading as shown in fig. 4a:

- 1) The bottom side of pressure sensor is set to a substrate temperature of 25°C.
- 2) The front side of the silicon cap is set to a higher temperature of 50°C due to the heat flow from the Peltier module.
- 3) The convection boundaries in the sidewalls of pressure sensor, silicon cap and TO8 package are set to be stagnant air (simplified case, 25°C).
- 4) The boundaries of pressure sensor and TO8 package are in contact with buffer solution and set to the solution temperature of 25°C.

The temperature distribution in fig. 4b reveals that the temperature difference mainly drops on the temperature-sensitive hydrogel while the pH-sensitive hydrogel keeps the same temperature as the substrate. To be specific, the temperature-sensitive hydrogel particles have a non-uniform temperature distribution: the top region of the hydrogel has a higher temperature than the bottom region. In this case, if the temperature is above the phase transition point, the hydrogel particles in the top region will shrink while those in the bottom side will still keep the previous shape. Meanwhile, the pH-sensitive hydrogel layer has a uniform temperature distribution, meaning that the whole hydrogel will swell at the same rate.

Fig. 4. Finite element simulation of the whole microsystem: (a) boundary conditions, (b) temperature distribution

4. EXPERIMENTS AND DISCUSSIONS

4.1 Sensor based on pH-sensitive hydrogel

The sensor based on pH-sensitive hydrogels in Fig. 5a comprises the pH-sensitive hydrogel, a modified TO8 package and the piezoresistive pressure sensor. When measuring solution flows through the inlet channels into the cavity of the pressure sensor, the hydrogel will raise its volume ΔV in response to the particular pH value and then deflect the membrane of the pressure sensor, consequently affecting the output voltage V_{out} . Fig. 5b reveals the sensor set-up, including the tubing pump (Ismatec, Germany), the buffer solutions (Merck, Germany), the pH sensor and the multimeter (Keithley, USA). The analyte solution was pumped into the pH sensor with a flow rate of 0.85mL/min. The multimeter collected the output voltage every 10 seconds.

Fig. 5. (a) Structure and (b) measuring set-up of the hydrogel-based pH sensor.

The measuring result of the pH sensor is depicted in Fig. 6. Since the hydrogel in dry state gets close to the membrane and deflects the membrane, the pH sensor has an offset voltage of 30 mV at the primary state. After being in contact with water, V_{out} raises to 120 mV sharply to reach its steady state. Then V_{out} reduces to 105 mV due to the restoring force of the membrane. Subsequently, pH 3 or pH 7 buffer solutions flow into the cavity and V_{out} alters proportionally with the pH value. After three cycles of pH change, V_{out} eventually reaches steady values. The response time t_{90} of the swelling/ deswelling process, when 90% of the final value at the steady state is reached, amounted to 50.5 min at the third cycle of the pH change (fig. 6b).

Fig. 6. Time-dependent sensor output voltage signal for pH steps between pH 3 and pH 7 with (a) three cycles and (b) the third cycle

4.2 Actuator based on temperature-sensitive hydrogels

The actuator based on temperature-sensitive hydrogel in fig. 7 comprises the temperature-sensitive hydrogel, a silicon cap, a hydrophilic Al_2O_3 membrane and the piezoresistive pressure sensor. A temperature chamber (Heraeus, Germany) provides heating to this thermal actuator.

Fig. 7. Structure of the Actuator based on temperature-sensitive hydrogels

The hydrogel conditioning is firstly performed (fig. 8a). Output voltage V_{out} drifts during the thermal cycles with varying temperatures between 30 and 40 °C. After 48 hours in room temperature, the sample takes the thermal dynamic measurement again. Even though the V_{out} drift still exists, the V_{out} difference between the thermal cycles is smaller than that in the primary experiment. When temperature increases from 30 to 45 °C in increments of 5 °C, V_{out} alters accordingly and reaches the steady state finally (fig. 8b). Fig. 8c highlights the difference between the temperature-decreasing and temperature-increasing curves. Meanwhile, V_{out} has a larger change in higher temperature region, revealing that the hydrogel in the actuator has a non-linear relationship between V_{out} and temperature T .

Fig. 8. Output signal V_{out} in response to temperature (a) during hydrogel conditioning and (b), (c) during step temperature measuring

4.3 Hydrogel-based pH sensor with force compensation

After being assembled completely, the sensor prototype is immersed into deionized (DI) water to verify the working principle. In step (I), the temperature-sensitive hydrogel remains dry while the pH-sensitive hydrogel comes in contact with DI water, swelling gradually with a positive sensing pressure ($p_{sens} > 0$) until it reaches the final steady state ($V_{out} = 135$ mV). Afterwards, this prototype is put into a vacuum chamber to remove the water. In this step (II), both hydrogels are kept dry without any pressure on the membrane of the pressure sensor. To compare the hydrogel's pressure value p_{comp} and p_{sens} , this prototype is immersed into the DI water completely at room temperature. The negative V_{out} demonstrates that the temperature-sensitive hydrogel has a higher pressure than the pH-sensitive hydrogel. In order to reach the balance state again, a higher temperature (e.g. 40 °C) was applied (step (IV)), causing the shrinkage of this temperature-sensitive hydrogel as well as the reduction of p_{comp} . During this steady state (fig. 9c), V_{out} varies between -15mV and 10 mV randomly, meaning that both hydrogels are in the dynamic balance. The response time t_{90} is 25 min (fig. 9d), which can be reduced by using a Peltier module with faster heating rate. The prototype will be tested in the pH buffer solution in the next step, using the same measuring condition as the sensor based on the pH-sensitive hydrogel.

Fig. 9. (a) Deflection of the membrane of the piezoresistive pressure sensor depending on the compensated pressure p_{comp} and sensing pressure p_{sens} from step (I) to (IV), V_{out} in response to temperature (b) through the whole measuring procedure, (c) during the sensor's balance state and (d) during the temperature adjustment

5. CONCLUSION

A force-compensated hydrogel-based pH sensor was presented in this paper. Compared to the conventional deflection method, this compensation method could reduce the response time. Firstly, Poly (N-isopropylacrylamide) (PNIPAAm) and poly (acrylic acid)-poly (vinyl alcohol) (PAA/PAA) copolymers were synthesized as temperature- and pH- sensitive hydrogels, respectively. Simulation results clearly demonstrated that the temperature difference mainly drops on the temperature-sensitive hydrogel while pH-sensitive hydrogel kept the same temperature as the substrate. A pH-sensitive micro-sensor and thermal micro-actuator were assembled into a miniaturized prototype. Following tests of this prototype in deionized water showed only half the response time of a sensor based on the conventional deflection method. All the experimental results confirm the applicability of the compensation method to the hydrogel-based microsensors. Future work will be performed to investigate this prototype's dynamic response on pH change. Besides, instead of the temperature chamber with low heating rate, the Peltier module will be utilized to increase the heating efficiency on the sensor and to achieve higher integration.

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